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(54) Title: AQUEOUS CLEANING AND DISINFECTING COMPOSITIONS BASED ON QUARTERNARY AMMONIUM COMPOUNDS AND ALKYLPOLYGLYCOSIDE SURFACTANTS

(57) Abstract

Aqueous disinfecting and cleaning compositions and concentrates which are efficacious against gram positive and gram negative bacteria, include a quaternary ammonium compound as its primary germicidal active agent, have a low content of active constituents, and do not include organic solvents such as alcohols, glycols, or glycol ethers in significant amounts.

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AQUEOUS CLEANING AND DISINFECTING COMPOSITIONS BASED ON QUARTERNARY AMMONIUM COMPOUNDS AND ALKYLPOLYGLYCOSIDE SURFACTANTS

The present invention relates to improvements in cleaning compositions. More particularly the present invention is directed to improved cleaning compositions which find particular use in hard surface cleaning and disinfecting applications.

Certain hard surface treatment compositions are known. For example, these include US 3539520 to Cantor et al., US 5454984 to Graubart et al., US Patent 4336151 to Like et al. as well as US Patent 5547990 to Hall et al. discusses certain classes of irritation mitigators in ceratinn hard surface treatment compositions.

Notwithstanding advantageous known art formulations, there yet remains a real and continuing need in the art for improved cleaning and disinfecting compositions in general, and in specific such compositions which provide at least one, but feature a plurality of the following characteristics: low volatile organic content, low irritancy to the end user of the composition, phase stability in storage (both at freeze-thaw, room temperature (i.e., 20°C) and elevated temperature (i.e., 40°C) conditions), ease of fabrication, low cost, efficacy against gram positive bacteria, efficacy against gram negative bacteria, good cleaning characteristics, and relatively low percentages actives required in such an aqueous formulation.

The compositions of the invention are aqueous disinfecting and cleaning compositions and concentrates thereof which are effective cleaning compositions and are efficacious as disinfecting compositions against gram positive and gram negative bacteria, have relatively low volatile organic content ("VOC") and are mild to the user of the compositions. That these results are concurrently achieved with a composition which includes a quaternary ammonium compound as its primary germicidal active agent is surprising, and indicates a synergistic effect not apparent from the prior art. These compositions also provide good cleaning and disinfecting properties with low amounts of active constituents, and according to certain preferred embodiments do not include organic solvents such as low molecular weight alcohols, glycols or glycol ethers, in significant amounts, i.e., amounts in excess of about 1%wt and more.

In accordance with a first aspect of the invention there is provided an aqueous disinfecting and cleaning composition in a concentrated form which exhibits reduced irritancy and which comprises (preferably, consists essentially of):

a disinfecting effective amount of a quaternary ammonium compound having germicidal properties, desirably present in an amount of from about 0.001 - 5% wt.;

a mitigating effective amount of at least one nonionic surfactant selected from alkylpolyglycoside compounds;

0.1 - 10%wt. of at least one further nonionic surfactant, preferably selected from alkoxylated primary alcohols;

0 - 3%wt. of a polymeric cationic surfactant based on a polyquaternary ammonium salt;

0 - 3%wt. of a builder, desirably present in an amount of about 0.1 - 0.5%wt.;

0 - 5%wt. of one or more conventional additives particularly coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents such as thickeners, pH adjusting agents and pH buffers including organic and inorganic salts; and,

water to form 100%wt. of the concentrate form of the inventive compositions.

In accordance with a second aspect of the invention there is provided an aqueous disinfecting and cleaning composition in a concentrated form which exhibits reduced irritancy which comprises (preferably consists essentially of):

a disinfecting effective amount of a quaternary ammonium compound having germicidal properties, desirably present in an amount of from about 0.001 - 5% wt.;

a mitigating effective amount of a binary surfactant system which comprises both (a) at least one nonionic surfactant selected from alkylpolyglycoside compounds, with (b) at least one further nonionic surfactant compound which is based on a polymeric alkylene oxide block copolymer, desirably present in an amount of from 0.1 – 10%wt.

0.1 – 10%wt. of at least one further nonionic surfactant, preferably selected from alkoxylated primary alcohols;

0 - 3%wt. of a polymeric cationic surfactant based on a polyquaternary ammonium salt;

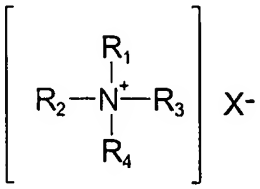
0 - 3%wt. of a builder, desirably present in an amount of about 0.1 - 0.5%wt.;

0 - 5%wt. of one or more conventional additives particularly coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents such as thickeners, pH adjusting agents and pH buffers including organic and inorganic salts; and,

water to form 100%wt. of the concentrate form of the inventive compositions.

In accordance with further preferred embodiments of the invention there are provided aqueous dilutions of the concentrated disinfecting and cleaning composition described above, which provides effective cleaning and sanitization.

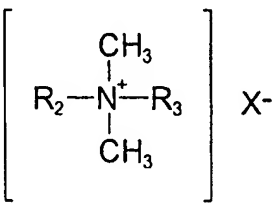
thereof include quaternary ammonium germicides which may be characterized by the general structural formula:



where at least one of R_1, R_2, R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radicals R_1, R_2, R_3 and R_4 may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ester linkages. The radical X may be any salt-forming anionic radical.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



wherein R_2 and R_3 are the same or different C_8-C_{12}alkyl, or R_2 is C_{12-16}alkyl, C_{8-18}alkylethoxy, C_{8-18}alkylphenolethoxy and R_3 is benzyl, and X is a halide, for example chloride, bromide or iodide, a

succinate, or may be methosulfate. The alkyl groups recited in R_2 and R_3 may be straight chained or branched, but are preferably substantially linear.

Particularly useful quaternary germicides include compositions which include a single quaternary, as well as mixtures of two or more different quaternaries. Particularly useful quaternary germicides include those commercially available under the BARDAC, BTC, BARQUAT, HYAMINE, tradenames (ex., Lonza AG, Stepan Co., or other commercial sources). These quaternary ammonium compounds may be used singly or in mixtures of two or more. These quaternary ammonium compounds are desirably present in the concentrate compositions in an amount of from about 0.001 - 5% wt., are desirably present in an amount of from 0.1 - 3%wt. and most desirably are present in an amount of from 0.5 – 3%wt. When diluted in a larger volume of water to form a cleaning and disinfecting composition, the quaternary ammonium compounds should be present in sufficient amount such that they are in a concentration of at least about 150 parts per million (p.p.m.), more desirably at least about 175 p.p.m. and most desirably about 200 – 250 p.p.m. The present inventors have surprisingly found that certain of their formulations exhibited effective cleaning and disinfecting with less than 200 p.p.m. of the quaternary ammonium compounds in cleaning compositions which is an amount below which is generally believed to be necessary for disinfecting efficacy.

The compositions of the invention also include a mitigating effective amount of at least one nonionic surfactant based on an alkylpolyglycoside compound. Exemplary suitable compounds include alkyl monoglycosides and polyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxylated glycosides and processes for making them are disclosed in U.S. Patent No. 2,974,134; U.S. Patent No.3,219,656; U.S. Patent No. 3,598,865; U.S. Patent No. 3,640,998; U.S. Patent No. 3,707,535; U.S. Patent No. 3,772,269; U.S. Patent No. 3,839,318; U.S. Patent No. 3,974,138; U.S. Patent No. 4,223,129; and U.S. Patent No. 4,528,106.

Exemplary alkyl glycoside surfactants suitable for use in the practice of this invention may be represented by formula I below:

$$RO{-}{-}(R_1O)_y{-}(G)_xZ_b$$

wherein:

R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to about 18 carbon atoms;

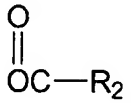
R_1 is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms, especially ethyl and propyl radicals;

y is a number which has an average value from about 0 to about 1 and is preferably 0;

G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and

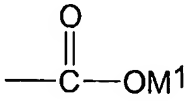
x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is selected O_2M^1,



$O(CH_2)$, CO_2M^1, OSO_3M^1, or $O(CH_2)SO_3M^1$; R_2 is $(CH_2)CO_2M^1$ or $CH=CHCO_2M^1$; with the proviso that Z can be O_2M^1 only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom,

$—CH_2OH$, is oxidized to form a



group);

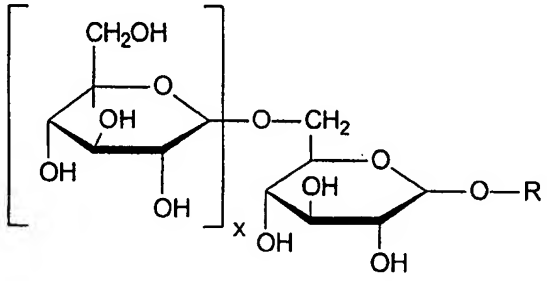
b is a number of from 0 to 3x+1 preferably an average of from 0.5 to 2 per glycosal group;

p is 1 to 10,

M^1 is H^+ or an organic or inorganic cation, such as, for example, an alkali metal, ammonium, monoethanolamine, or calcium.

As defined in Formula I above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms.

Most preferably, the inventive compositions include an alkylpolyglycoside compound according to the structure:



wherein:

R is an alkyl group, preferably a linear alkyl chain, which comprises C_8 to C_{16} alkyl groups;

x is an integer value of from 0 – 3, inclusive.

Examples of such alkylpolyglycoside compounds according to this structure include: where R is comprised substantially of C_8 and C_{10} alkyl chains yielding an average value of about 9.1 alkyl groups per molecule (Glucopon® 220 UP, Glucopon® 225 DK); where R is comprised of C_8, C_{10}, C_{12}, C_{14} and C_{16} alkyl chains yielding an average value of about 10.3 alkyl groups per molecule (Glucopon® 425); where R is comprised substantially of C_{12}, C_{14} and C_{16} alkyl chains yielding an average value of about 12.8 alkyl groups per molecule (Glucopon® 600 UP, Glucopon® 625 CSUP, and Glucopon® 625 FE, all of which are available from Henkel Corp., Ambler PA.) Also useful as the alkylpolyglycoside compound is Triton® CG-110 (Union Carbide Corp.).

Further examples of commercially available alkylglycosides as described above include, for example, Glucopon® 325N which is described as being a 50% C_9-C_{11} alkyl polyglycoside, also commonly referred to as D-glucopyranoside (from Henkel Corp, Ambler PA). Particularly preferred as the alkylpolyglycoside compounds are those illustrated in the Examples.

The inclusion of the alkylpolyglycoside compound to the compositions significantly reduces the irritation potential of the aqueous compositions as compared to like compositions which however omit this constituent. Only now have the present inventors discovered that compositions, especially those according to particularly preferred embodiments of the present invention, which further include the alkylpolyglycoside compound as a necessary constituent have even further reduced ocular irritation potential. While not wishing to be bound by the following, it is theorized that the presence of both a nonionic surfactant constituent based on a compound other than an alkylpolyglycoside in conjunction with the nonionic surfactant based on the alkylpolyglycoside compound have a synergistic or complementary effect in reducing the irritation potential of such aqueous compositions. When both are present, as in the first embodiment of the invention, the former to the latter are desirably included in relative weight ratios of from 3:1 to 1.5:1. This irritation mitigating effect has also been found in the inventive compositions according to the second aspect of the invention, wherein there is present the binary surfactant system which comprises at least one nonionic surfactant selected from alkylpolyglycoside compounds, and at least one further nonionic surfactant compound which is based on a polymeric alkylene oxide block copolymer. According to this second embodiment of the invention, generally good results have been observed when the weight ratio of the alkylpolyglycoside compounds to the polymeric alkylene oxide block copolymer are in respective ratios of from 0.5:1 – 2:1.

The amounts of the nonionic surfactant based on an alkylpolyglycoside compound to the compositions may vary in accordance with the level of irritancy mitigation sought. Generally, the alkylpolyglycoside surfactant may be included in any amount which mitigates irritancy. Good efficacy is found when present from about 0.01 – 10%wt. based on the total weight of the composition, but amounts

of from 0.1 – 7%wt. and preferably from about 0.5 – 4%wt. are preferred. It is to be understood that the amount which is to be included will vary upon several factors such as the amounts of the other constituents present in a composition, as well as the irritancy levels of such other constituents. The optimal amount of the alkylpolyglycoside surfactant to be included may be determined by routine experimentation, such as by the method outlined with reference to the Examples.

In compositions according to the second aspect of the invention, the amounts of the two surfactants which comprise the binary surfactant system may vary in accordance with the level of irritancy mitigation sought. Generally, the at least one nonionic surfactant selected from alkylpolyglycoside compounds is present from about 0.01 – 9.99%wt., but is preferably present from 0.01 – 4%wt., and at the same time the nonionic surfactant compound based on the polymeric alkylene oxide block copolymer may also be present in amounts of from 0.01 – 9.99%wt, but preferably is present in an amount of from 0.5 – 2%wt. The optimal amounts of the two surfactants which make up the binary surfactant system which are to be included in the inventive compositions may be determined by routine experimentation, such as by the method outlined with reference to the Examples. While not wishing to be bound by the following, it is believed that the presence of the alkylpolyglycoside compounds with the polymeric alkylene oxide block copolymer compounds provide a synergistic improvement with respect to the mitigation of the level of irritancy, particularly the ocular irritancy of the inventive compositions.

By way of non-limiting example, useful nonionic surfactants based on polymeric alkylene oxide block copolymers which are included in the second aspect of the invention, include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C_2-C_4 alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, and can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols.

One group of such useful nonionic surfactants containing the characteristic alkylene oxide blocks are those which may be generally represented by the formula (A):

$$HO—(EO)_x(PO)_y(EO)_z—H \qquad (A$$

where EO represents ethylene oxide,

PO represents propylene oxide,

y equals at least 15,

$(EO)_{x+z}$ equals 20 to 50% of the total weight of said compounds, and,

the total molecular weight is preferably in the range of about 2000 to 15,000.

Another group of nonionic surfactants appropriate for use in the new compositions can be represented by the formula (B):

$$R—(EO,PO)_a(EO,PO)_b—H \qquad (B$$

wherein R is an alkyl, aryl or aralkyl group, where the R group contains 1 to 20 carbon atoms, the weight percent of EO is within the range of 0 to 45% in one of the blocks a, b, and within the range of 60 to 100% in the other of the blocks a, b, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block.

Further nonionic surfactants which in general are encompassed by Formula B include butoxy derivatives of propylene oxide/ethylene oxide block polymers having molecular weights within the range of about 2000-5000.

Still further useful nonionic surfactants containing polymeric butoxy (BO) groups can be represented by formula (C) as follows:

$$RO—(BO)_n(EO)_x—H \qquad (C$$

wherein R is an alkyl group containing 1 to 20 carbon atoms,

n is about 5-15 and *x* is about 5-15.

Also useful as the nonionic block copolymer surfactants, which also include polymeric butoxy groups, are those which may be represented by the following formula (D):

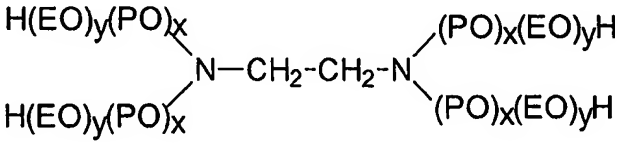
$$HO—(EO)_x(BO)_n(EO)_y\text{-}H \qquad (D)$$

wherein n is about 5-15, preferably about 15,

x is about 5-15, preferably about 15, and

y is about 5-15, preferably about 15.

Still further useful nonionic block copolymer surfactants include ethoxylated derivatives of propoxylated ethylene diamine, which may be represented by the following formula:



(E

where (EO) represents ethoxy,

(PO) represents propoxy,

the amount of $(PO)_x$ is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of $(EO)_y$ is such as to provide about 20% to 90% of the total weight of said compound.

Of these, the most preferred are those which are represented by formula (A) above. Such materials include those available in the PLURONIC series, and in particular the PLURONIC "F", "L", "P"

and "R" series of block copolymers of propylene oxide and ethylene oxide (ex BASF) Generally those of the PLURONIC L series and the PLURONIC R series are preferred as these are supplied in liquid form by the manufacturer and are readily formulated into the present inventive compositions. These are also available in a wide range of HLB values, and those having HLB values in the range of 1.0 - 23.0 may be used, although those with intermediate HLB values such as from about 12.0 - 18.0 are found to be particularly advantageous.

Other useful exemplary nonionic block copolymers based on a polymeric ethoxy/propoxy units which may also be used include those presently commercially available in the POLYTERGENT E, and POLYTERGENT P series of block copolymers (ex. Olin Corp.) These are described to be nonionic surfactants based on ethoxy/propoxy block copolymers, conveniently available in a liquid form from its supplier.

The inventive compositions further include at least one further nonionic surfactant which provides a further detersive benefit to the inventive compositions. Preferred nonionic surfactants provide surprisingly good levels of cleaning performance, particularly in conjunction with the preferred quaternary ammonium compounds described herein.

One class of nonionic surfactants are alkoxylated (i.e., ethoxylated, propoxylated, etc.) alcohols. These include the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 2 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide, tridecanol condensed with about 6 to moles of ethylene oxide, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with a distillation or separation fraction of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of ethylene oxide per mole of total alcohol or about 9 moles of ethylene oxide per mole of alcohol and tallow alcohol ethoxylates containing 6 ethylene oxide to 11 ethylene oxide per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the NEODOL ethoxylates (ex Shell Chemical Co.); which are higher aliphatic, primary alcohols containing about 9-15 carbon atoms, i.e., C_{11} alkanol condensed with 7 moles of ethylene oxide (NEODOL 1-7), C_9-C_{11} alkanol condensed with an average of 2.5 moles of ethylene oxide (NEODOL 91-2.5); C_9-C_{11} alkanol condensed with 6 moles of ethylene oxide (NEODOL 91-6), C_9-C_{11} alkanol condensed with 8 moles of ethylene oxide (NEODOL 91-8), C_{12-13} alkanol condensed with 6.5 moles ethylene oxide (NEODOL 23-6.5), C_{12-13} alkanol condensed with 7 moles ethylene oxide (NEODOL 23-7), C_{12-15} alkanol condensed with 7 moles of ethylene oxide

(NEODOL 25-7), C_{12-15} alkanol condensed with 9 moles ethylene oxide (NEODOL 25-9), C_{12-15} alkanol condensed with 12 moles ethylene oxide (NEODOL 25-12), C_{14-15} alkanol condensed with 13 moles ethylene oxide (NEODOL 45-13), and the like. Of these, the most preferred material is a C_{12-15} alkanol condensed with 7 moles of ethylene oxide.

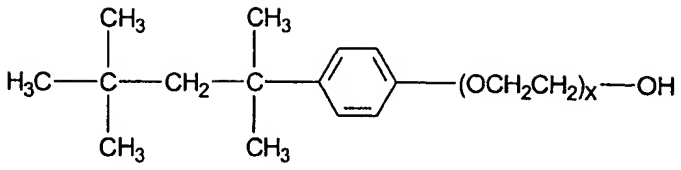
A further class of nonionic surfactants which are advantageously present in the inventive compositions are those presently marketed under the GENAPOL tradename (ex. Clariant). Particularly useful are those in the GENAPOL "26-L" series which include for example: C12-16 linear alcohols condensed with with varying amounts of ethylene oxide.

Additional useful nonionic surfactants include those based on alcohol and ethylene oxide condensates of a secondary aliphatic alcohol. Such are available in the TERGITOL series of surfactants (ex. Union Carbide Corp.) These alcohols contain 8 to 18 carbon atoms in a straight or branched chain configuration and are condensed with 5 to 30 moles of an alkylene oxide, especially ethylene oxide. Examples of commercially available nonionic surfactants of this type are C_{11}-C_{15} secondary alkanols condensed with varying amounts of ethylene oxide. For example, these include TERGITOL 15-S-9 with an average of 9 ethylene oxides per alkanol, TERGITOL 15-S-7 with an average of 7 ethylene oxides per alkanol, as well as TERGITOL 15-S-12 with an average of 12 ethylene oxides per alkanol.

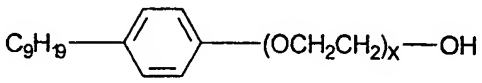
Further useful nonionic surfactants include certain alkoxylated linear aliphatic alcohol surfactants which are believed to be the condensation products of a C_8-C_{10} hydrophilic moiety with alkylene oxides, especially polyethylene oxide and or polypropylene oxide moieties. Such alkoxylated linear alcohol surfactants are presently commercially available under the tradename POLYTERGENT (ex. Olin Chemical Co., Stamford CT). Of these particularly useful are those which are marketed as POLYTERGENT SL-22, POLYTERGENT SL-42, POLYTERGENT SL-62 and POLYTERGENT SL-29, of which POLYTERGENT SL-62 is particularly advantageous. POLYTERGENT SL-92 is described as being a moderately foaming, biodegradable alkoxylated linear alcohol surfactant having on average 8 moles of oxyethylene groups per molecule. These alkoxylated linear alcohol surfactants provide good detersive action in the removal of many types of fats and greases such as are frequently found in soils on hard surfaces, as well as providing a further solubilizing effects and may be included in the concentrate compositions according to the present invention with advantage.

The preferred alkoxylated linear alcohol surfactants also exhibit low levels of ocular irritation in the concentrate compositions.

Further useful nonionic surfactants include alkoxylated, and particularly ethoxylated octyl and nonyl phenols according to the following general structural formulas:



or,



in which the C_9H_{19} group in the latter formula is a mixture of branched chained isomers. In both formulae, x indicates an average number of ethoxy units in the side chain. Suitable non-ionic ethoxylated octyl and nonyl phenols include those having from about 7 to about 13 ethoxy units. Such compounds are commercially available under the trade name TRITON (ex. Union Carbide, Danbury CT).

Exemplary alkoxylated alkyl phenols useful as a nonionic surfactant also include certain compositions presently commercially available from the Rhône-Poulenc Co., (Cranbury, NJ) under the general trade name IGEPAL, which are described to be octyl and nonyl phenols. These specifically include IGEPAL CO730 which is described as an ethoxylated nonyl phenol having an average of 15 ethoxy groups per molecule.

These nonionic surfactant compounds described above may be used singly or in mixtures. When present, these further nonionic surfactants comprise 0.01 - 10%wt. of the concentrate compositions, desirably comprise 0.1 - 8%wt. and most desirably comprise about 2 - 6%wt. and especially about 5%wt. of the concentrate compositions taught herein.

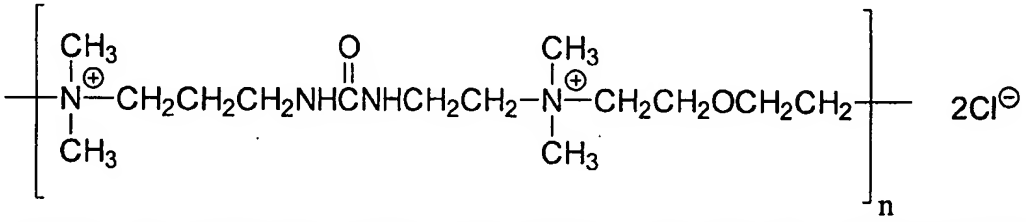
The inventive compositions optionally but desirably include a builder. Such a builder constituent may be present in an amount of from 0 - 3%wt. but preferably 0.1 – 0.5%wt. based on the total weight of the concentrate compositions taught herein. Such include water soluble inorganic builders which can be used alone, in admixture with other water soluble inorganic builders, as well as in conjunction with one or more organic alkaline sequestrant builder salts.

Exemplary builders include alkali metal carbonates, phosphates, polyphosphates and silicates. More specific examples include sodium tripolyphosphate, sodium carbonate, sodium bicarbonate, sodium tetraborate, potassium carbonate, sodium polyphosphate, potassium pyrophosphate, potassium tripolyphosphate, and sodium hexametaphosphate. Further exemplary builders also include organic alkaline sequestrant builder salts such as alkali metal polycarboxylates including water-soluble citrates such as sodium and potassium citrate, sodium and potassium tartarate, sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylene diamine triacetates, sodium and potassium nitrilotriacetates, as well as sodium and potassium tartrate mono- and di-succinates.

Also useful are gluconate or glucoheptonate salts particularly sodium gluconate and sodium glucoheptonate. Particularly advantageously used are di-, tri- and tetrasodium salts of ethylenediaminetetraacetic acid, especially tetrasodium salts thereof. As noted, these organic builder salts may be used individually, as a combination of two or more organic builder salts, as well as in conjunction with one or more detergency builders, including those indicated above. It is to be understood that many of these builder materials also provide a useful pH stabilizing effect in the compositions in which they form a part.

As is noted above, the compositions according to the invention are aqueous in nature. Water is added to the constituents in order to provide 100% by weight of the composition. The water may be tap water, but is preferably distilled or deionized water. The composition of the invention generally comprise at least 80%wt. water.

An optional but in some compositions, desirable constituent is a cationic polymeric polyquaternary ammonium salt, especially a halogen salt such as a chloride salt. Such a material is one which includes at least one repeating monomer unit wherein such monomer includes as part of its structure a quaternary ammonium. A particularly useful class of such materials are those sold under the trade designation MIRAPOL and are available from Rhône-Poulenc Surfactant & Specialty Chemicals Co. (Cranbury, NJ). These materials are highly cationic in nature, and are believed to be in accordance with the following general structure:



wherein n is an integer or 2 or greater, and is desirably in the range of 2 - 12, more desirably is about 6. Such a material is commercially available as MIRAPOL A-15. This material may be present to from 0 - 3%wt., desirably from 0.01 –3%.

The inventors have found that the inclusion of such material provides a useful soil suspending benefit which is desirable from a cleaning standpoint, although it has also been observed by the inventors that inclusion of such a material may have a detrimental effect on the disinfecting properties of the compositions.

The specific constituents which may be used in the compositions according to the invention are per se, known to the art.

The inventive compositions are useful in the disinfecting and/or cleaning of surfaces, especially hard surfaces in need of such treatment. These in particular include surfaces wherein the presence of gram

positive and/or gram negative bacteria are suspected. In accordance with the present inventive process, cleaning and/or disinfecting of such surfaces comprises the step of applying a stain releasing and a disinfecting effective amount of a composition as taught herein to such a stained surface. Afterwards, the compositions are optionally but desirably wiped, scrubbed or otherwise physically contacted with the hard surface, and further optionally, may be subsequently rinsed from such a cleaned and disinfected hard surface.

Such a hard surface cleaning and disinfecting composition according to the invention is may be provided as a ready to use product which may be directly applied to a hard surface, but is desirably provided in a concentrated form intended to be diluted in water to form a cleaning composition therefrom.

Exemplary hard surfaces include surfaces composed of refractory materials such as: glazed and unglazed tile, porcelain, ceramics as well as stone including marble, granite, and other stones surfaces; glass; metals; plastics e.g. polyester, vinyl; fiberglass, and other hard surfaces known to the industry.

The hard surface cleaner composition provided according to the invention can be also be provided as a ready to use product in a manually operated spray dispensing container. Such a typical container is generally made of synthetic polymer plastic material includes spray nozzle, a dip tube and associated pump dispensing parts and is thus ideally suited for use in a consumer "spray and wipe" application.

In a yet a further embodiment, the compositions according to the invention may be formulated so that it may be useful in conjunction with a "aerosol" type product wherein it is discharged from a pressurized aerosol container. If the inventive compositions are used in an aerosol type product, it is preferred that corrosion resistant aerosol containers such as coated or lined aerosol containers be used. Known art propellants such as liquid propellants as well as propellants of the non-liquid form, i.e., pressurized gases, including carbon dioxide, air, nitrogen, hydrocarbons as well as others may be further included in the compositions.

The compositions described herein may be used without further dilution, but may also be used with a further aqueous dilution, i.e., in concentrate composition: water concentrations of 1:0, to extremely dilute dilutions such as 1:1000. When subjected to further aqueous dilution, such a dilution is preferably a weight or volume ratio proportion of from 1:10 - 1:64, and most desirably is about 1:64. The actual dilution selected is in part determinable by the degree and amount of dirt and grime to be removed from a surface(s), the amount of mechanical force imparted to remove the same, as well as the observed efficacy of a particular dilution.

Conversely, nothing in the specification shall be also understood to limit the forming of a "super-concentrated" cleaning composition based upon the composition described above. Such a super-

concentrated composition is essentially the same as the compositions described above except in that they include a lesser amount of water.

Other conventional optional additives, although not particularly elucidated herein may also be included in the present inventive compositions. Exemplary optional conventional additives include but are not limited to: pH adjusting agents and pH buffers including organic and inorganic salts; non-aqueous solvents, perfumes, perfume carriers, optical brighteners, coloring agents such as dyes and pigments, opacifying agents, hydrotropes, antifoaming agents, viscosity modifying agents such as thickeners, enzymes, anti-spotting agents, anti-oxidants, anti-corrosion agents as well as others not specifically elucidated here. These should be present in minor amounts, preferably in total comprise less than about 5% by weight of the compositions, and desirably less than a total weight of about 3%wt.

Example Formulations:

Preparation of Example Formulations:

Exemplary formulations illustrating certain preferred embodiments of the inventive compositions and described in more detail in Table 1 below were formulated generally in accordance with the following protocol.

Into a suitably sized vessel, a measured amount of water was provided after which the constituents were added in no specific or uniform sequence, which indicated that the order of addition of the constituents was not critical. All of the constituents were supplied at room temperature, and any remaining amount of water was added thereafter. Certain of the nonionic surfactants if gels at room temperature were first preheated to render them pourable liquids prior to addition and mixing. Mixing of the constituents was achieved by the use of a mechanical stirrer with a small diameter propeller at the end of its rotating shaft. Mixing, which generally lasted from 5 minutes to 120 minutes was maintained until the particular exemplary formulation appeared to be homogeneous. The exemplary compositions were readily pourable, and retained well mixed characteristics (i.e., stable mixtures) upon standing for extend periods. The compositions of the example formulations are listed on Table 1. The weight percentages indicated the "as supplied" weights of the named constituent.

As is indicated, to all of the formulations of Table 1 was added sufficient deionized water in "quantum sufficient" to provide 100 parts by weight of a particular formulation.

Table 1		
	Comp.1	Ex.1
NEODOL 25-7	5.00	--
POLYTERGENT SL-62	--	4.00
BTC 8358 (80%)	1.625	1.625
PLURONIC L64	2.0	--
GLUCOPON 325N (50%)	--	4.0
EDTA (38%)	0.25	0.25
Fragrance	0.20	0.20
Dye Solution	0.20	0.20
DI water	q.s.	q.s.

The identity of the constituents of Table 1 above are described in more detail on Table 2, below, including the "actives" percentage of each were a constituent was not 100%wt. "actives".

TABLE 2	
constituent:	identity:
PLURONIC L-64	nonionic ethoxy/propoxy block copolymer surfactant (BASF Corp.)
NEODOL 25-7	nonionic C12-15 alkanol condensed with 7 moles ethylene oxide (Shell Chemical Co.)
POLYTERGENT SL-62	alkoxylated alcohol (BASF Inc.)
GLUCOPON 325N (50%)	technical grade mixture of C9-11 alkylpolyglycosides (Henkel Corp.)
BTC 8358 (80%)	alkyl dimethyl benzyl ammonium chloride (Stepan Co.)
EDTA (38%)	tetrasodium ethylenediaminetetraacetate
Fragrance	proprietary composition
dye solution	proprietary composition
DI water	deionized water

Evaluation of Antimicrobial Efficacy:

Several of the exemplary formulations described in more detail on Table 1 above were evaluated in order to evaluate their antimicrobial efficacy against *Staphylococcus aureus* (gram positive type pathogenic bacteria) (ATCC 6538), and *Salmonella choleraesuis* (gram negative type pathogenic bacteria) (ATCC 10708) The testing was performed in accordance with the protocols outlined in "Use-Dilution Method", Protocols 955.14, 955.15 and 964.02 described in Chapter 6 of "Official Methods of Analysis",

16th Edition, of the Association of Official Analytical Chemists; "Germicidal and Detergent Sanitizing Action of Disinfectants", 960.09 described in Chapter 6 of "Official Methods of Analysis", 15th Edition, of the Association of Official Analytical Chemists; or American Society for Testing and Materials (ASTM) E 1054-91 the contents of which are herein incorporated by reference. This test is also commonly referred to as the "AOAC Use-Dilution Test Method".

As is appreciated by the skilled practitioner in the art, the results of the AOAC Use-Dilution Test Method indicates the number of test substrates wherein the tested organism remains viable after contact for 10 minutes with at test disinfecting composition / total number of tested substrates (cylinders) evaluated in accordance with the AOAC Use-Dilution Test. Thus, a result of "0/60" indicates that of 60 test substrates bearing the test organism and contacted for 10 minutes in a test disinfecting composition, 0 test substrates had viable (live) test organisms at the conclusion of the test. Such a result is excellent, illustrating the excellent disinfecting efficacy of the tested composition. Results for lesser amount of test substrates such as for 10, 20, 30 or 40 test substrates provide useful screening results, although insufficient to satisfy the requirement of 60 test substrates as dictated by the AOAC Use-Dilution Test.

Results of the antimicrobial testing are indicated on Table 3, below. The reported results indicate the number of test cylinders with live test organisms/number of test cylinders tested for each example formulation and organism tested.

Table 3

Formulation:	*Staphylococcus aureus*	*Salmonella choleraesuis*
Comp.1	0/30	0/30
Ex.1	0/60	1/60

Evaluation of Ocular Irritation:

The ocular irritation characteristics of formulations according to the invention were evaluated using the known Draize Eye test protocol. Evaluation was performed on several formulations according to the invention and described more fully in Table 1 above.

As known to those skilled in the art, the Draize Eye Test measures eye irritation for the grading of severity of ocular lesions, measuring three dimensions: scores obtained for the cornea, iris and conjunctiva. For the cornea, after exposure to the composition, A the cornea opacity is graded on a scale from 1 to 4; B the area of cornea involved is graded on a scale from 1-4 (where the score = A x B x 5 may be a total maximum of 80). For evaluation of the iris, after exposure the composition, A the involvement of the iris is graded on a scale of 1-2 (where the score = A x 5 may be a total maximum of 10). For a evaluation of the conjunctive, A Redness is graded on a scale of 1-3; B Chemosis is graded on a scale of 1-

4; and C Discharge is measured on a scale of 1-3 [where the score = (A + B + C) x 2 may be a maximum of 20]. The maximum total score is the sum of all scores obtained for the cornea, iris and conjunctive (a maximum of 110).

The results of the Draize test are reported below. These indicate that an EPA classification Category "3" was appropriate, where corneal involvement or irritation cleared in 21 days or less. These results are in accordance with the guidelines of the Environmental Protection Agency (EPA), 40 C.F.R. Ch.1, §162.10, (1986).

Table 4

Formulation:	Corneal opacity in test subjects / number of days
Control 1	8.33 / 21
Ex.1	0 / 21

As may be seen from these results, the composition according to Ex. 1 exhibited very low levels of ocular irritation, as is demonstrated by the rapid rate at which corneal opacity cleared in the test subjects.

Evaluation of Cleaning Efficacy:

Various formulations amongst those listed above were evaluated for their cleaning efficacy on tile surfaces utilizing the following protocols. "Standard soiled tiles" were prepared for use in the tests. These were prepared in accordance with the protocol described in ASTM 4488-87, Annex A5 "Particulate and Oily Soil/Vinyl Tiles Test Method". This preparation of standard soiled tiles and cleaning protocol was performed for certain of cleaning compositions formed from the formulations described in more detail on Table 1.

Evaluation was performed utilizing a Gardner Washability Apparatus, using a standard soil tiles prepared in accordance with the protocol described above at a standard pressure and sponge stroke settings in order to determine or quantify the cleaning efficiency of the formulations. These formulations were used formed into a cleaning composition wherein 1 part of a formulation of Table 1 was diluted with 64 parts water. For comparative purposes, a 1:64 dilution of a commercially available concentrated cleaning and disinfecting preparation, Lysol® Deodorizing Cleaner "Country Scent" variety was also prepared and evaluated in the same test. In determining the cleaning efficiency of each of the formulations, reflectance values were determined using a Minolta Chromameter where each tile was measured three times and the mean reflectance value are reported below on Table 5. For each of these tiles, there were at least four replicates, each of which were evaluated and used to determine the mean reflectance value of Table 5. Testing was performed for each of the following: a clean unsoiled tile, a soiled tile, and a soiled tile

following Gardner Washability Apparatus scrubbing. Such reflectance values were then employed to calculate cleaning efficiency according to the following formula:

$$\text{Cleaning Efficiency} = \frac{Lt - Ls}{Lo - Ls}$$

wherein:

Lt = reflectance average after scrubbing solid tile;

Ls = reflectance average before cleaning soiled tile;

Lo = reflectance average original tile before soiling.

The evaluation procedure noted above was performed in groups of test tiles, wherein the cleaning compositions formed from formulations according to Table 1 were compared to a tiles treated with the cleaning composition formed using a commercially available product, LYSOL Deodorizing Cleaner "Country Scent" formulation (Reckitt & Colman Inc., Montvale NJ). These cleaning efficiency results are shown in the Table 5, following.

Table 5

Formulation:	Oily
LYSOL Deodorizing Cleaner "Country Scent" formulation	45 – 50%
Comp.1	35 – 40%
Ex.1	50 – 55%

As shown, the measurement of the cleaning effectiveness of the test samples involved the ability of the cleaning composition to remove the test soil from the test substrate. This was expressed by Cleaning Efficiency; as numerical values for a Cleaning Efficiency increase, higher cleaning effectiveness is achieved for the cleaning composition tested. As the results show, the inventive composition showed excellent cleaning characteristics which favorably compare to the commercially available products.

Claims:

1. Aqueous disinfecting and cleaning composition in a concentrated form which exhibits reduced irritancy which comprises,
a disinfecting effective amount of a quaternary ammonium compound having germicidal properties;
a mitigating effective amount of at least one nonionic surfactant selected from alkylpolyglycoside compounds;
0.1 – 10%wt. of a nonionic surfactant;
0 - 3%wt. of a polymeric cationic surfactant based on a polyquaternary ammonium salt;
0 - 3%wt. of a builder 0 - 5%wt. of one or more conventional additives particularly coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents such as thickeners, pH adjusting agents and pH buffers including organic and inorganic salts; and,
water to form 100%wt. of the concentrate form of the inventive compositions.

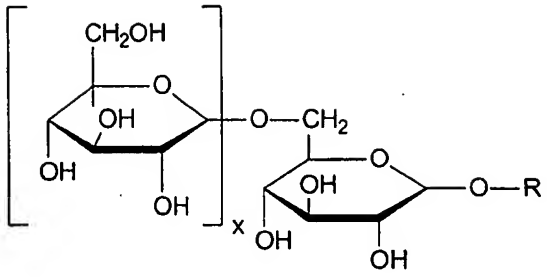
2. An aqueous disinfecting and cleaning composition according to claim 1 wherein the quaternary ammonium compound having germicidal properties is present in an amount of from about 0.001 - 5% wt.

3. An aqueous disinfecting and cleaning composition according to claim 1or 2 wherein the at least one further nonionic surfactant is present in an amount of from about at 0.1 – 8%wt.

4. An aqueous disinfecting and cleaning composition according to claim 3 wherein the at least one further nonionic surfactant is an alkoxylated primary alcohol.

5. An aqueous disinfecting and cleaning composition according to claim 3 wherein the at least one further nonionic surfactant is a polymeric alkylene oxide block copolymer.

6. An aqueous disinfecting and cleaning composition according to claim 1 which comprises an alkylpolyglycoside compound according to the structure:



wherein:

R is an alkyl group, preferably a linear alkyl chain, which comprises C_8 to C_{16} alkyl groups;

x is an integer value of from 0 – 3, inclusive

7. An aqueous composition which comprises 1 part of the aqueous disinfecting and cleaning concentrate composition according to any of claims 1 though 6 per 10 to 64 parts water.

8. Aqueous disinfecting and cleaning composition in a concentrated form which exhibits reduced irritancy according to claim 1 which comprises:

a disinfecting effective amount of a quaternary ammonium compound having germicidal properties;

a mitigating effective amount of a binary surfactant system which comprises both (a) at least one nonionic surfactant selected from alkylpolyglycoside compounds, with (b) at least one further nonionic surfactant compound which is based on a polymeric alkylene oxide block copolymer;

0.1 - 10%wt. of at least one further nonionic surfactant;

0 - 3%wt. of a polymeric cationic surfactant based on a polyquaternary ammonium salt;

0 - 3%wt. of a builder;

0 - 5%wt. of one or more conventional additives particularly coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents such as thickeners, pH adjusting agents and pH buffers including organic and inorganic salts; and,

water to form 100%wt. of the concentrate form of the inventive compositions.

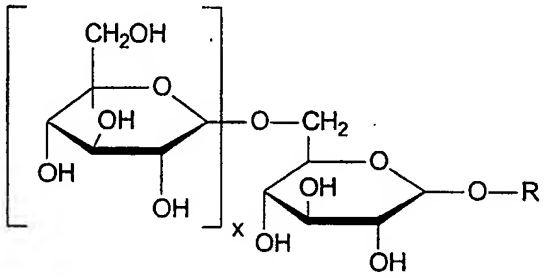
9. An aqueous disinfecting and cleaning composition according to claim 8 wherein the quaternary ammonium compound having germicidal properties is present in an amount of from about 0.001 - 5% wt.

10. An aqueous disinfecting and cleaning composition according to claim 8 or 9 wherein the binary surfactant system is present in an amount of from 0.1 – 10%wt.

11. An aqueous disinfecting and cleaning composition according to claim 8 which comprises at least one further nonionic surfactant.

12. An aqueous disinfecting and cleaning composition according to claim 11 wherein the at least one further nonionic surfactant is an alkoxylated primary alcohol.

13. An aqueous disinfecting and cleaning composition according to claim 8 which comprises an alkylpolyglycoside compound according to the structure:



wherein:

R is an alkyl group, preferably a linear alkyl chain, which comprises C_8 to C_{16} alkyl groups;

x is an integer value of from 0 – 3, inclusive

14. An aqueous composition which comprises 1 part of the aqueous disinfecting and cleaning concentrate composition according to any of claims 8 - 13 per 10 to 64 parts water.

15. A process for cleaning and/or disinfecting of hard surfaces which comprises the step of:

applying an effective amount of a composition according to claim 1 to the surface.

16. A process for cleaning and/or disinfecting of hard surfaces which comprises the step of:

applying an effective amount of a composition according to claim 8 to the surface.

INTERNATIONAL SEARCH REPORT

Inter. ional Application No
PCT 99/05960

A. CLASSIFICATION OF SUBJECT ER
IPC 6 C11D1/835 C11D3/48 A01N25/02 A01N33/12 A01N25/30
//C11D1/62,C11D1/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 98 24314 A (RECKITT & COLMAN INC) 11 June 1998 (1998-06-11) claim 1; example 56	1-3,5-7
X	EP 0 698 660 A (KAO CORP) 28 February 1996 (1996-02-28)	1-4,6, 15,16
A	example 14	8-14
X	US 5 576 284 A (VAN BUSKIRK GREGORY ET AL) 19 November 1996 (1996-11-19)	1-4,6,7, 14-16
A	column 6, line 1 - line 9; example 12	5,8-13
X	WO 86 05199 A (STALEY MFG CO A E) 12 September 1986 (1986-09-12)	1-3,6,7, 14-16
A	claims 1,2; table I	8-11,13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 July 1999	29/07/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Inte. .tional Application No
PCT/ 99/05960

C.(Continuation) DOCUMENTS CO RED TO BE RELEVANT

Category ³	Citation of document, with indication,where appropriate. of the relevant passages	Relevant to claim No.
X	WO 95 31962 A (GOJO IND INC) 30 November 1995 (1995-11-30)	1-4,6
A	claims 1,4; table XIV	8-13
A	WO 94 05753 A (HENKEL CORP) 17 March 1994 (1994-03-17) claim 1; example 1	1,2,6-9, 13-16

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter onal Application No
PCT/ 99/05960

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
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			AU	5092993	A	29-03-1994
			CA	2142896	A	17-03-1994
			CZ	9500600	A	15-11-1995
			EP	0659204	A	28-06-1995
			JP	8501122	T	06-02-1996
			MX	9305470	A	31-03-1994
			PL	307863	A	26-06-1995
			RU	2093550	C	20-10-1997